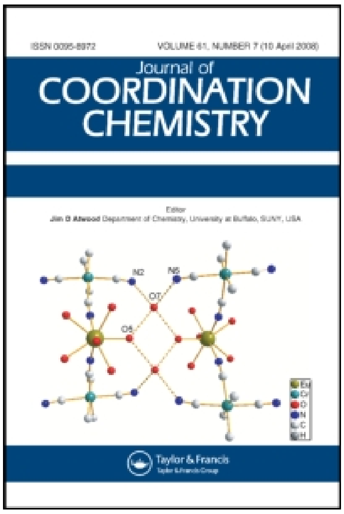

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PREPARATION OF TERTIARY AND DITERTIARY PHOSPHINE DERIVATIVES OF $(\mu\text{-RSe})_2Fe_2(CO)_6$ VIA CO SUBSTITUTION. THE CRYSTAL STRUCTURE OF $(\mu\text{-PhSe})_2Fe_2(CO)_4(Ph_2PCH\ \ CHPPh_2)$

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PREPARATION OF TERTIARY AND DITERTIARY PHOSPHINE DERIVATIVES OF (μ-RSe)$_2$Fe$_2$(CO)$_6$ VIA CO SUBSTITUTION. THE CRYSTAL STRUCTURE OF (μ-PhSe)$_2$Fe$_2$(CO)$_4$(Ph$_2$PCH$=$CHPPh$_2$)

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Reaction of (μ-PhSe)$_2$Fe$_2$ (CO)$_6$ with Ph$_3$P and Ph$_2$MeP in refluxing benzene afforded *mono*-substituted derivatives (μ-PhSe)$_2$Fe$_2$(CO)$_5$L (**1a**, L$=$Ph$_3$P; **1b**, L$=$Ph$_2$MeP), whereas reaction in refluxing toluene gave symmetrically *bis*-substituted derivatives (μ-PhSe)$_2$Fe$_2$(CO)$_4$L$_2$(**2a**, L$=$Ph$_3$P; **2b**, L$=$Ph$_2$MeP); Reaction of (μ-ArSe)$_2$Fe$_2$(CO)$_6$(Ar$=$Ph, p-MeC$_6$H$_4$) with Ph$_2$PCH$_2$CH$_2$PPh$_2$ in refluxing toluene gave symmetrically substituted ditertiary phosphine-bridged derivatives (μ-ArSe)$_2$Fe$_2$ (CO)$_4$ (Ph$_2$PCH$_2$CH$_2$PPh$_2$) (**3a**, Ar $=$ Ph; **3b**, Ar $=$ p-MeC$_6$H$_4$), while Ph$_2$PCH $=$ CHPPh$_2$ in benzene yielded non-symmetrically substituted chelated derivatives (μ-ArSe)$_2$Fe$_2$ (CO)$_4$ (Ph$_2$PCH $=$CHPPh$_2$) (**4a**, Ar $=$ Ph; **4b**, Ar $=$ p-MeC$_6$H$_4$), in which the diphosphine is coordinated to a single iron atom. Structures of the above derivatives have been elucidated by IR and NMR (^{1}H, ^{13}C and ^{77}Se) spectroscopy; the molecular structure of **4a** was confirmed by X-ray diffraction techniques. It crystallizes in the monoclinic space group $P2_1/c$ with a = 21.908(3), b = 17.207(2), c = 23.954(2) Å, β = 114.24(1)°, V = 8234 Å^3 X, Z = 4 and Dc = 1.501 g/cm^3; final R = 0.060 for 3941 observed reflections.

Keywords: CO; substitution; tertiary phosphine; selenolato-complexes; X-ray structure

INTRODUCTION

Although CO substitutions of thiolato-bridged complexes (μ-RS)$_2$Fe$_2$(CO)$_6$ and (μ-RS)(μ-R′S)Fe$_2$(CO)$_6$ by tertiary phosphines have been extensively studied,[1–6] corresponding reactions of selenolato-bridged complexes (μ-RSe)$_2$Fe$_2$(CO)$_6$ are

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so far very little explored.[7] To compare the substitution reactivity of the CO ligand in those bridged complexes and to prepare new derivatives of selenolato-bridged complexes, an investigation of the reactions of $(\mu\text{-RSe})_2Fe_2(CO)_6$ ($R{=}Ph$, $p\text{-}MeC_6H_4$) with tertiary phosphines Ph_3P, Ph_2MeP, $Ph_2PCH_2CH_2PPh_2$ and $Ph_2PCH{=}CHPPh_2$ was undertaken. Herein we describe the synthesis and characterization of several new tertiary and ditertiary phosphine derivatives and the single-crystal structure of one ditertiary phosphine derivative, $(\mu\text{-PhSe})_2Fe_2(CO)_4(Ph_2PCH{=}CHPPh_2)$, **4a**.

EXPERIMENTAL

All reactions were carried out under an atmosphere of highly pre-purified tank nitrogen. Benzene and toluene were distilled under nitrogen from sodium/benzophenone ketyl and purged with nitrogen prior to use. Triphenylphosphine, methyldiphenylphosphine, 1, 2-*bis*(diphenylphosphinyl)ethane and *cis*-1, 2-*bis*(diphenylphosphinyl)ethylene were chemical reagents purchased from Strem Chemicals Inc.; $(\mu\text{-PhSe})_2Fe_2(CO)_6$ and $(\mu\text{-}p\text{-}MeC_6H_4Se)_2Fe_2(CO)_6$ were obtained according to published methods.[8–9]

The progress of reactions was monitored by thin layer chromatography. Column chromatography was carried out with a 300 × 25 mm column using 200–300 mesh silica gel. Solid products were recrystallized from deoxygenated 1:1 CH_2Cl_2 and hexane at –20°C.

Melting points are uncorrected. Microanalyses were performed on a Perkin Elmer 240C instrument. IR spectra were recorded on a Nicolet FT-IR 5DX spectrophotometer using KBr discs. ^1H, ^{13}C and ^{77}Se NMR spectra were recorded on JEOL FX-90Q and Bruker ARX-500 NMR spectrometers.

Preparation of 1a-b

A 100 cm^3 Schlenk flask equipped with a stir bar and a nitrogen inlet tube was charged with 0.296 g (0.5 mmol) of $(\mu\text{-PhSe})_2Fe_2(CO)_6$, 0.157 g (0.6 mmol) of triphenylphosphine and 30 cm^3 of benzene. The mixture was stirred at reflux for 3 h. Solvent was removed *in vacuo* and the residue was subjected to column chromatography. First, a mixture of petroleum ether and CH_2Cl_2(v/v = 9/1) eluted a minor orange band, which was not collected. Further elution with a mixture of petroleum ether and CH_2Cl_2 (v/v = 3/1) yielded a major red band, from which 0.193 g (47%) of **1a** was obtained as red crystals after recrystallization. M.p. 118–119°C; anal., calcd for $C_{35}H_{25}Fe_2O_5PSe_2$: C, 50.88; H, 3.05%;

found: C, 51.14; H, 3.55%; IR (KBr disc): $\nu_{C\equiv O}$ 2041 (vs), 1975 (vs), 1926 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ) : 6.52–7.76 (m, 25H, $5C_6H_5$) ppm; ^{77}Se NMR ($CDCl_3$, Me_2Se_2, δ) : 297.58 (s) ppm.

A similar reaction using 0.11 cm^3 (0.6 mmol) methyldiphenylphosphine instead of triphenylphosphine was carried out to afford 0.347 g (98%) of **1b** as red crystals after recrystallization. M. p. 118–120°C; anal., calcd. for $C_{30}H_{23}Fe_2O_5PSe_2$: C, 47.16; H, 3.03%; found: C, 47.01; H, 3.17%; IR (KBr disc) : $\nu_{C\equiv O}$ 2032(vs), 1983 (*vs*), 1934(*vs*) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 2.08 (d, J=7.2Hz, 3H, CH_3), 6.78–7.94 (m, 20H, $4C_6H_5$) ppm.

Preparation of 2a-b

To a flask as described above was added 0.296 g (0.5 mmol) of (μ-PhSe)$_2$Fe$_2$(CO)$_6$, 0.392 g (1.5 mmol) of triphenylphosphine and 50 cm^3 of toluene. The mixture was stirred at reflux for 6 h. Solvent was removed *in vacuo* and the residue was subjected to column chromatography. A mixture of CH_2Cl_2 and petroleum ether (v/v = 1/4) eluted a red band, from which 0.251 g (41%) of **1a** was obtained. Further elution with a mixture of CH_2Cl_2 and petroleum ether (v/v = 2/3) yielded a dark red band, from which 0.209 g (39%) of **2a** was obtained as dark red crystals after recrystallization. M.p. 166–168°C; anal., calcd for $C_{52}H_{40}Fe_2O_4P_2Se_2$: C, 58.90; H, 3.80%; found: C, 58.84; H, 3.86%; IR (KBr disc) : $\nu_{C\equiv O}$ 1983(vs), 1936(m), 1918 (vs) cm^{-1} 10; $^{-1}$H NMR ($CDCl_3$, δ): 6.52–7.80 (m, 40H, $8C_6H_5$) ppm; ^{77}Se NMR ($CDCl_3$, Me_2Se_2, δ): 215.76(s), 273.31(s) ppm.

The same procedure as that described above for **2a** was used in the preparation of **2b**, except for using 0.22 cm^3 (1.2 mmol) of methyldiphenylphosphine instead of triphenylphosphine. The reaction gave 0.204 g(53%) of **1b** and 0.182 g(39%) of **2b** as dark red solids. M. p. 146–147°C; anal., calcd. for $C_{42}H_{36}Fe_2O_4P_2Se_2$: C, 53.88; H, 3.88%; found: C, 53.55; H, 3.75%; IR(KBr disc) : $\nu_{C\equiv O}$ 1983(vs), 1942 (m), 1918(vs) cm^{-1}; ^{1}H NMR ($CDCl_3$, δ): 2.28 (d, J=7.2Hz, 6H, $2CH_3$), 6.46–8.00 (m, 30H, $6C_6H_5$) ppm.

Preparation of 3a-b

To a flask as described above was added 0.296 g (0.5 mmol) of (μ-PhSe)$_2$Fe$_2$(CO)$_6$, 0.199 g (0.5 mmol) of $Ph_2PCH_2CH_2PPh_2$ and 30 cm^3 of toluene. The mixture was stirred at reflux for 2 h. After removal of the solvent *in vacuo* the residue was subjected to column chromatography. First, petroleum ether eluted a minor orange band, which was not collected. Further elution with a mixture of CH_2Cl_2/petroleum ether (v/v = 1/1) yielded a major red band, from which 0.177 g (38%) of **3a** was obtained as red crystals after recrystallization. M.p. 236–237°C; anal., calcd for $C_{42}H_{34}Fe_2O_4P_2Se_2$: C, 53.99; H, 3.67%; found: C, 53.65; H, 4.10%; IR(KBr disc): $\nu_{C\equiv O}$ 1984(s), 1952(vs), 1924(s), 1897(m) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 2.20–2.80 (m, 4H, $2CH_2$), 6.96 – 8.16 (m, 30H, $6C_6H_5$) ppm; ^{77}Se NMR ($CDCl_3$, Me_2Se_2, δ): 243.01(s), 320.31(t, J = 250Hz) ppm.

The same procedure as that described above for **3a** was used in the preparation of **3b**, except for using 0.301 g (0.5 mmol) of (μ-*p*-$MeC_6H_4Se)_2Fe_2(CO)_6$ instead of (μ-$PhSe)_2Fe_2(CO)_6$. The reaction gave 0.172 g (36%) of **3b** as red crystals after recrystallization. M.p. 242–244°C; anal., calcd. for $C_{44}H_{38}Fe_2O_4P_2Se_2$: C, 54.92; H, 3.98%; found: C, 54.92; H, 3.87%; IR(KBr disc): $\nu_{C\equiv O}$ 1983(s), 1950(vs), 1918(s), 1893(vs) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 2.12, 2.30(s, s, 6H, $2CH_3$), 2.35–2.50(m, 4H, $2CH_2$), 6.70–7.88(m, 28H, $4C_6H_5$, $2C_6H_4$); ^{13}C NMR ($CDCl_3$, δ): 21.07 (m, CH_3), 24.81, 25.01 (s, s, $2CH_2$),128–139 (m, $4C_6H_5$, $2C_6H_4$), 216.24–216.28(m, 4CO) ppm; ^{77}Se NMR ($CDCl_3$, Me_2Se_2, δ): 239.05(s), 313.09 (t, J = 268Hz) ppm.

Preparation of 4a-b

To a flask as described above was added 0.296 g (0.5 mmol) of (μ-$PhSe)_2Fe_2(CO)_6$, 0.224 g (0.6 mmol) of $Ph_2PCH{=}CHPPh_2$ and 30 cm^3 of benzene. The mixture was stirred at reflux for 2 h. Solvent was removed *in vacuo* and the residue was subjected to column chromatography. First, petroleum ether eluted a minor orange band, which was not collected. Then, a mixture of CH_2Cl_2/petroleum ether (v/v = 1/1) eluted a major red band, from which 0.361 g (81%) of **4a** was isolated as black crystals after recrystallization. M.p. 162–163°C; anal., calcd for $C_{42}H_{32}Fe_2O_4P_2Se_2 \cdot 0.36CH_2Cl_2$: C, 52.87; H, 3.43%; found: C, 52.42; H, 3.41%; IR(KBr disc): $\nu_{C\equiv O}$ 2008(vs), 1950(vs), 1926(s) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 5.36(s, 0.36 × 2H, CH_2Cl_2), 6.58(d, J = 7.2Hz, 2H, 2CH), 6.80–7.88(m, 30H, $6C_6H_5$) ppm; ^{77}Se NMR ($CDCl_3$, Me_2Se_2, δ): 223.55(s), 324.01(d, J = 490Hz) ppm.

The same procedure as that described above for **4a** was used in the preparation of **4b**, except that 0.301 g (0.5 mmol) of (μ-*p*-$MeC_6H_4Se)_2Fe_2(CO)_6$ was used instead of (μ-$PhSe)_2Fe_2(CO)_6$. Some 0.405 g (84%) of **4b** was produced as black crystals after recrystallization. M.p. 162–164°C; anal., calcd. for $C_{44}H_{36}Fe_2O_4P_2Se_2$: C, 55.03; H, 3.78%; found: C, 55.32; H, 3.81%; IR(KBr disc): $\nu_{C\equiv O}$ 2016(vs), 1950 (vs), 1909(s) cm^{-1}; ^1H NMR ($CDCl_3$, δ): 1.92, 1.97 (s, s, 6H, $2CH_3$), 6.11–7.84 (m, 30H, 2CH, $4C_6H_5$, $2C_6H_4$) ppm; ^{13}C NMR ($CDCl_3$, δ): 20.87, 20.99(s, s, $2CH_3$), 127–140(m, $4C_6H_5$, $2C_6H_4$, 2CH), 151.19–151.90(m, CO), 212.89 (s, 3CO) ppm; ^{77}Se NMR ($CDCl_3$, Me_2Se_2, δ): 222.10(s), 314.73(d, J = 560Hz) ppm.

Single crystal structural determination of 4a

Crystals of **4a** suitable for X-ray diffraction were obtained by recrystallization from CH_2Cl_2/hexane in a refrigerator. A black crystal measuring 0.3 × 0.2 × 0.2 mm was mounted on a glass fibre and placed on a Rigaku-AFC 7R diffractometer fitted with a graphite monochromator. A total of 7541 independent reflections were collected at room temperature with MoKα (λ = 0.71069 Å) radiation by the ω-2θ scan mode. Of these, 3941 independent reflections with $I>3s(I)$ were considered to be observed and were used in subsequent refinement. Data were corrected for Lp factors. Crystal data are listed in Table I.

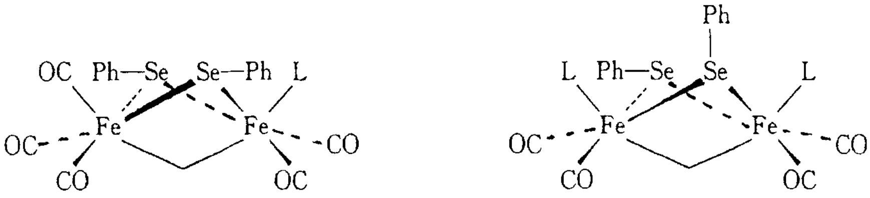
TABLE I Crystal data and details of structure refinement for 4a

Formula	$C_{84}H_{60}O_8P_4Se_4Fe_4$
Formula Weight	1860. 52
Crystal Colour, Habit	black, prismatic
Crystal System	monoclinic
Space Group	$P2_1/c$ (# 14)
a (Å)	21. 908(3)
b (Å)	17. 207(2)
c (Å)	23. 954(2)
β(°)	114. 24(1)
Z	4
Dc(g · cm^{-3})	1. 501
F(000)	3712. 00
μ(cm^{-1})	25.89
Data collected	7813
Unique data	7451
Data with $I\geq3\sigma(I)$	3941
R	0.060
R_w	0.067
(ρ)max (eÅ^{-3})	1.2

The structure was solved by direct methods and Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined. The final refinement by full-matrix least-squares method for non-hydrogen atoms converged to unweighted and weighted agreement factors of 0.060 (R) and 0.067 (R_w). The highest peak in the final difference Fourier map was 1.2e/ Å.^{3} All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation.

RESULTS AND DISCUSSION

It has been found that one equivalent of selenolato-bridged compound (μ-PhSe)$_2$Fe$_2$(CO)$_6$ reacted with tertiary phosphine Ph$_3$P or Ph$_2$MeP in benzene at reflux to afford mono-substituted derivatives (μ-PhSe)$_2$Fe$_2$(CO)$_5$(Ph$_3$P) (**1a**) and (μ-PhSe)$_2$Fe$_2$(CO)$_5$(Ph$_2$MeP) (**1b**), respectively (Scheme 1). Owing to the greater steric hindrance of Ph$_3$P the yield of **1a** is much lower than that of **1b**. For example, reaction with PPh$_3$ for 3 h gave **1a** in 47% yield, whereas reaction with Ph$_2$MeP for 3 h afforded **1b** in essentially quantitative yield. Similarly, *bis*-substituted derivatives (μ-PhSe)$_2$Fe$_2$(CO)$_4$(Ph$_3$P)$_2$(**2a**) and (μ-PhSe)$_2$Fe$_2$(CO)$_4$–(Ph$_2$MeP)$_2$ **2b**) (Scheme 1) were obtained in 39% yield by refluxing a mixture of 1:3 (μ-PhSe)$_2$Fe$_2$(CO)$_6$ and the tetiary phosphine Ph$_3$P or Ph$_2$MeP in toluene, along with the corresponding mono-substituted derivatives **1a** (41%) and **1b** (53%), respectively.



1a L=Ph$_3$P
1b L=Ph$_2$MeP

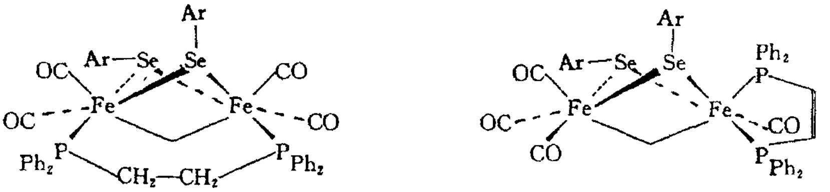
2a L=Ph$_3$P
2b L=Ph$_2$MeP

Scheme 1

Derivatives **1a–b** (**1a** was previously reported, but with incomplete characterization data)[7] and **2a–b** were well characterized by elemental analysis, IR and ^{1}H(^{77}Se) NMR spectroscopies. ^{1}H NMR spectra exhibited the presence of corresponding organic groups and the IR spectra showed three absorption bands in the range 2041 - 1918 cm^{-1}, characteristic of the terminal carbonyls attached to iron atoms. It is worth noting that $\nu_{C\equiv O}$ value of the derivatives, compared to the parent complex (μ-PhSe)$_2$Fe$_2$(CO)$_6$(2065, 2024, 1991, 1975 cm^{-1}),[8] have shifted considerably to lower frequences. For example, for mono-substituted derivatives **1a–b**, the highest energy $\nu_{C\equiv O}$ bands decrease by 24 cm^{-1} and 33 cm^{-1} respectively, whereas for *bis*-substituted derivatives **2a–b**, the highest energy $\nu_{C\equiv O}$ bands decrease by 82 cm^{-1}. Obviously, this should be attributed to the strong electron-releasing effects of tertiary phosphines, which can enhance dπ-pπ back-bonding between the iron atom and the carbon atom of the carbonyl groups, and in turn reduce the bond order of the terminal carbonyls.[10]

In addition, since the axial CO ligands are more reactive than equatorial ones in similar nucleophilic substitutions of thiolato-bridged complexes (this had been confirmed by crystal structures of corresponding tertiary phosphine substituted derivatives, such as (μ-cyclo-$C_6H_{11}S$)(μ-*n*-$C_5H_{11}S$)Fe_2 $(CO)_5$ (PPh_3)[5] and (μ-*i*-C_3H_7S) (μ-$PhCH_2S$) Fe_2 $(CO)_4$ $(PPh_3)_2$)[6]), the tertiary phosphine ligand L in **1a–b** and **2a–b** would be reasonably proposed as being located in an axial position.

Further study showed that the selenolato-bridged complexes (μ-PhSe)$Fe_2(CO)_6$ and (μ-*p*-$MeC_6H_4Se)_2Fe_2(CO)_2$ might react with ditertiary phosphine Ph_2PCH_2. CH_2PPh_2 in toluene at reflux to give symmetrically substituted, bridged species **3a–b** (Scheme 2). Analysis, IR and $^1H(^{13}C,\ ^{77}Se)$ NMR spectra are in good agreement with the structures shown in Scheme 2. For instance, the IR spectra of **3a–b**, similar to those of *bis*-substituted **2a–b**, showed four absorption bands for terminal carbonyls in the range 1984 – 1893 cm^{-1}. The highest energy $\nu_{C\equiv O}$ bands for **3a–b**, as compared with respective parent complexes (μ-PhSe)$Fe_2(CO)_6$ and (μ-*p*-$MeC_6H_4Se)_2Fe_2(CO)_6$(2065, 2032, 2000, 1967 cm^{-1})[9] decrease by 81 and 82 cm^{-1}, respectively.



3a Ar=Ph
3b Ar=P-MeC_6H_4

4a Ar=Ph
4b Ar=P-MeC_6H_4

Scheme 2

This implies that **3a–b** are *bis*-substituted derivatives. However, in contrast to **2a–b** derived from a monophosphine, the ditertiary phosphine ligand in **3a–b** has displaced two less reactive equatorial carbonyls in order to avoid strong steric repulsions involving two μ-ArSe ligands with the supposed *endo*-ditertiary phosphine $Ph_2PCH_2CH_2PPh_2$. In ^1H NMR spectrum of **3b** there are two *p*-Me signals, at δ 2.12 and 2.30 ppm, which means that the two *p*-$CH_3C_6H_4$ groups attached to Se atoms are in *anti* positions.

More interestingly, (μ-ArSe)$_2Fe_2(CO)_6$ (Ar=Ph, *p*-MeC_6H_4) reacted with another ditertiary phosphine $Ph_2PCH{=}CHPPh_2$ in refluxing benzene to afford non-symmetrically substituted, chelated compounds **4a–b** in 81% and 84% yields, respectively (Scheme 2). The structures shown in Scheme 2 are also in good agreement with analyses, IR and ^1H (^{13}C, ^{77}Se) NMR data. The differences between the structures of **3a–b** and **4a–b** are reflected in the IR and ^{13}C spectra:

(i) in the IR spectra the highest energy $\nu_{C\equiv O}$ of **4a–b**, as compared with those of parent complexes, shifted toward lower frequencies by only 57 and 49 cm^{-1}, whereas those of **3a–b** shifted by 81 and 82 cm^{-1}, as mentioned above. These values coincide very well with **4a–b** having an unsubstituted Fe $(CO)_3$ unit and with **3a–b** having a *bis*-substituted $Fe(CO)_2$ (diteritary phosphine) $Fe(CO)_2$ structural unit; (ii) the ^{13}C spectrum of **3b** showed one multiplet (with small $^2J_{P-C}$) at about δ 216 ppm, assigned to the carbonyls in the structural unit $[(CO)_2FePPh_2CH_2]_2$, whereas that of **4b** showed one multiplet (also with small $^2J_{P-C}$) at about δ 151 ppm, assigned to the carbonyl attached to ditertiary phosphine-chelated iron atom and one singlet at about 213 ppm, assigned to the carbonyls in the unsubstituted $Fe(CO)_3$ group.

In addition, in a similar way to **3b**, the *p*-MeC_6H_4 groups of **4b** should be attached to Se atoms in *anti* positions since its ^1H NMR spectrum showed two singlets at δ 1.92 ppm and δ 1.97 ppm for two *p*-CH_3 substituents.

In order to elucidate the orientations of the aryl groups attached to Se atoms and to further establish the structures of the derivatives mentioned above, the ^{77}Se NMR spectra of **1a, 2a, 3a–b, 4a–b** along with parent complex $(\mu\text{-}PhSe)_2Fe_2(CO)_6$ were recorded. ^{77}Se NMR showed that the parent complex contains two kinds of Se atoms, which are bonded to two aryl groups in *anti* positions. This is because the spectrum of the parent complex showed two singlets, one at δ 318.03 ppm and the other at 276.66 ppm. For the mono-Ph_3P substituted derivative **1a**, the ^{77}Se NMR spectrum showed one singlet at δ 297.58 ppm. This indicates that there is only one kind of Se atom both attached to *syn* phenyl groups (for **1a** another *syn* isomer, which has two *endo* phenyl groups, could not exist due to strong steric repulsion between the two aryl groups) and thus the isomer conversion from *anti* to *syn* occured during nucleophilic substitution of the parent complex. However, for the *bis*-Ph_3P-substituted derivative **2a**, the ^{77}Se NMR spectrum showed two singlets at δ 273.31 and 215.76 ppm, which clearly indicates that no isomer conversion occured during substitution and the two phenyl groups remain in *anti* positions. It should be pointed out that the two ^{77}Se values, compared to those of the parent complex shifted upfield about 44 ppm and 61 ppm due to the electron-releasing effects of the two Ph_3P ligands. Different from **1a** and **2a**, the ^{77}Se NMR spectrum of **3a** showed one singlet at δ 243.01 ppm and one triplet at δ 320.31 ppm ($^2J_{P-SE}$ = 250 Hz), while that of **3b** showed one singlet at 239.05 ppm and one triplet at 313.09 ppm ($^2J_{P-SE}$ = 268Hz). These data are in good agreement with the symmetrically substituted structures having two *anti* aryl groups. The downfield triplet is assigned to the Se atom close to the two P atoms of the ditertiary phosphine, whereas the upfield singlet is assigned to the Se atom remote from the ditertiary phosphine.

The ^{77}Se NMR spectra for **4a–b** are in accordance with the non-symmetrically substituted, chelated structures having two *anti* aryl groups. The spectra showed one singlet upfield (δ 223.55 ppm for **4a** and δ 222.10 ppm for **4b**) and one doublet downfield [δ 324.01 ppm ($^2J_{P\text{-}SE}$ = 490 Hz) for **4a** and δ 314.73 ppm ($^2J_{P\text{-}SE}$ = 560 Hz) for **4b**]. The downfield doublet for **4a** or **4b** is assigned to the Se atom close to the P atom in an equatorial position. Similar coupling interactions between phosphorus and selenium were also observed in the case of (μ-PhSe) [μ-CPhSe(i-Pr)P]$Fe_2(CO)_6$.[12]

In order to unequivocally confirm the structure of **4a**, an X-ray diffraction analysis was undertaken. Table II lists atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms. Although there are two crystallographically independent molecules in the asymmetric unit, only one set of bond lengths and one set of angles are listed in Tables III and IV, respectively. This is because the two independent molecules are essentially the same, slight differences being within experimental error. Figure 1 shows the molecular structure.

TABLE II Fractional coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms of 4a

Atom	*x/a*	*y/b*	*z/c*	*Beq*
Se(1)	0.0248(1)	−0.0042(1)	0.20688(9)	3.14(5)
Se(2)	−0.1139(1)	−0.0811(1)	0.12867(9)	3.18(5)
Se(3)	0.5534(1)	0.2341(1)	0.24894(9)	3.74(6)
Se(4)	0.6164(1)	0.2004(1)	0.15502(9)	3.61(6)
Fe(1)	−0.0073(1)	−0.1373(1)	0.1887(1)	2.76(7)
Fe(2)	−0.0260(1)	−0.0387(2)	0.1003(1)	3.25(8)
Fe(3)	0.5349(1)	0.1302(2)	0.1762(1)	3.12(7)
Fe(4)	0.5206(2)	0.2766(2)	0.1459(1)	3.73(9)
P(1)	−0.0022(3)	−0.1824(3)	0.2770(2)	3.2(1)
P(2)	−0.0406(3)	−0.2549(3)	0.1516(2)	3.3(1)
P(3)	0.4510(3)	0.0853(3)	0.1957(2)	3.5(2)
P(4)	0.5903(3)	0.0243(3)	0.2195(2)	3.4(1)
O(1)	−0.0833(9)	−0.1259(9)	-0.0146(7)	6.9(5)
O(2)	0.1026(8)	−0.0559(9)	0.0925(7)	5.7(5)
O(3)	0.1258(7)	−0.1937(8)	0.2135(6)	4.4(4)
O(4)	−0.0678(9)	0.1188(9)	0.0501(8)	8.1(6)
O(5)	0.4760(7)	0.0655(8)	0.0546(6)	4.6(4)
O(6)	0.4555(9)	0.264(1)	0.0135(7)	8.0(5)
O(7)	0.3871(9)	0.3045(10)	0.1385(8)	7.1(6)
O(8)	0.573(1)	0.4341(9)	0.1558(8)	8.4(6)
C(1)	−0.062(1)	−0.093(1)	0.031(1)	5.0(7)
C(2)	0.052(1)	−0.047(1)	0.0969(7)	2.5(5)
C(3)	0.074(1)	−0.170(1)	0.2041(9)	3.2(6)
C(4)	−0.055(1)	0.058(1)	0.0688(10)	5.2(7)
C(5)	−0.016(1)	−0.322(1)	0.2175(9)	4.6(6)
C(6)	0.003(1)	−0.290(1)	0.2721(9)	4.0(6)
C(7)	0.118(1)	0.015(1)	0.2310(9)	4.1(5)
C(8)	0.140(1)	0.075(1)	0.2047(9)	5.2(5)

TABLE II (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	*Beq*
C(9)	0.209(1)	0.090(1)	0.226(1)	6.3(6)
C(10)	0.254(1)	0.049(1)	0.270(1)	7.0(6)
C(11)	0.235(1)	−0.011(1)	0.2987(10)	6.2(6)
C(12)	0.166(1)	−0.027(1)	0.2785(9)	5.3(5)
C(13)	0.0730(10)	−0.155(1)	0.3455(8)	3.5(4)
C(14)	0.126(1)	−0.205(1)	0.3682(10)	5.4(5)
C(15)	0.184(1)	−0.177(2)	0.419(1)	8.4(7)
C(16)	0.188(1)	−0.104(2)	0.442(1)	7.2(6)
C(17)	0.132(1)	−0.058(1)	0.4196(10)	5.9(6)
C(18)	0.073(1)	−0.081(1)	0.3696(9)	4.4(5)
C(19)	−0.0689(9)	−0.1785(10)	0.3057(8)	2.8(4)
C(20)	−0.054(1)	−0.197(1)	0.3655(9)	5.0(5)
C(21)	−0.107(2)	−0.198(2)	0.384(1)	8.4(7)
C(22)	−0.170(2)	−0.183(2)	0.347(1)	8.6(8)
C(23)	−0.185(1)	−0.169(1)	0.288(1)	6.5(6)
C(24)	−0.133(1)	−0.166(1)	0.2679(9)	4.6(5)
C(25)	−0.1407(10)	0.009(1)	0.1637(8)	3.8(4)
C(26)	−0.116(1)	0.019(1)	0.2255(9)	4.2(5)
C(27)	−0.143(1)	0.086(1)	0.2481(9)	5.5(5)
C(28)	−0.186(1)	0.132(1)	0.207(1)	6.0(6)
C(29)	−0.207(1)	0.123(1)	0.1493(10)	5.3(5)
C(30)	−0.185(1)	0.059(1)	0.1228(8)	4.4(5)
C(31)	−0.1300(10)	−0.279(1)	0.1096(8)	3.7(4)
C(32)	−0.167(1)	−0.302(1)	0.1397(9)	5.4(5)
C(33)	−0.237(1)	−0.316(1)	0.108(1)	7.9(7)
C(34)	−0.263(1)	−0.311(1)	0.044(1)	6.0(6)
C(35)	−0.228(1)	−0.288(1)	0.014(1)	6.5(6)
C(36)	−0.156(1)	−0.272(1)	0.0473(9)	5.1(5)
C(37)	−0.0043(10)	−0.304(1)	0.1049(8)	3.6(4)
C(38)	−0.011(1)	−0.386(1)	0.0936(10)	5.7(6)
C(39)	0.015(1)	−0.425(1)	0.0581(10)	5.9(6)
C(40)	0.049(1)	−0.383(1)	0.0314(9)	5.6(6)
C(41)	0.058(1)	−0.301(1)	0.0398(9)	5.1(5)
C(42)	0.032(1)	−0.263(1)	0.0791(8)	4.2(5)
C(43)	0.5009(10)	0.091(1)	0.1053(9)	2.9(6)
C(44)	0.484(1)	0.267(1)	0.067(1)	5.5(7)
C(45)	0.443(1)	0.292(1)	0.1435(9)	4.3(7)
C(46)	0.555(1)	0.374(1)	0.1535(9)	4.9(7)
C(47)	0.531(1)	−0.042(1)	0.2348(8)	3.6(6)
C(48)	0.471(1)	−0.014(1)	0.2239(8)	3.8(6)
C(49)	0.647(1)	0.262(1)	0.3005(9)	4.1(5)
C(50)	0.672(1)	0.230(1)	0.3585(10)	5.1(5)
C(51)	0.736(1)	0.251(1)	0.3998(10)	5.7(6)
C(52)	0.774(1)	0.300(1)	0.383(1)	6.1(6)
C(53)	0.747(1)	0.333(1)	0.325(1)	6.0(6)
C(54)	0.683(1)	0.313(1)	0.2815(9)	4.8(5)
C(55)	0.471(1)	0.111(1)	0.3163(10)	5.1(5)
C(56)	0.463(1)	0.146(1)	0.365(1)	6.8(6)
C(57)	0.411(1)	0.197(1)	0.349(1)	7.0(6)
C(58)	0.373(1)	0.218(1)	0.293(1)	7.6(7)
C(59)	0.381(1)	0.181(1)	0.2445(9)	5.4(5)
C(60)	0.4311(10)	0.129(1)	0.2557(8)	3.6(4)
C(61)	0.3668(9)	0.074(1)	0.1340(8)	3.1(4)
C(62)	0.346(1)	0.111(1)	0.0795(9)	4.4(5)

TABLE II (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	*Beq*
C(63)	0.284(1)	0.099(1)	0.0328(9)	4.4(5)
C(64)	0.242(1)	0.049(1)	0.0428(10)	5.3(5)
C(65)	0.260(1)	0.010(1)	0.097(1)	7.1(6)
C(66)	0.322(1)	0.024(1)	0.1462(10)	5.5(5)
C(67)	0.6131(6)	0.181(1)	0.0750(8)	3.4(4)
C(68)	0.617(1)	0.241(1)	0.0390(9)	5.1(5)
C(69)	0.619(1)	0.229(1)	−0.018(1)	6.7(6)
C(70)	0.623(1)	0.156(1)	−0.036(1)	6.5(6)
C(71)	0.622(1)	0.093(1)	0.001(1)	5.9(6)
C(72)	0.6178(10)	0.106(1)	0.0553(9)	4.0(5)
C(73)	0.6171(10)	−0.038(1)	0.1725(8)	2.9(4)
C(74)	0.5660(10)	−0.078(1)	0.1257(8)	3.5(4)
C(75)	0.581(1)	−0.122(1)	0.0832(8)	4.3(5)
C(76)	0.644(1)	−0.126(1)	0.0875(8)	4.2(5)
C(77)	0.695(1)	−0.088(1)	0.1335(9)	4.4(5)
C(78)	0.680(1)	−0.043(1)	0.1757(8)	4.2(5)
C(79)	0.665(1)	0.025(1)	0.2915(9)	4.2(5)
C(80)	0.673(1)	−0.023(1)	0.338(1)	6.2(6)
C(81)	0.733(2)	−0.025(2)	0.390(1)	8.2(7)
C(82)	0.780(1)	0.025(1)	0.394(1)	6.7(6)
C(83)	0.777(1)	0.076(1)	0.352(1)	5.4(5)
C(84)	0.716(1)	0.078(1)	0.2998(10)	5.5(5)

TABLE III Selected bond lengths (Å) for 4a

atom	*atom*	*distance*	*atom*	*atom*	*distance*
Se(1)	Fe(1)	2.383(3)	Se(1)	Fe(2)	2.403(3)
Se(1)	C(7)	1.91(2)	Se(2)	Fe(1)	2.388(3)
Se(2)	Fe(2)	2.403(4)	Se(2)	C(25)	1.96(2)
P(1)	C(6)	1.86(2)	P(1)	C(13)	1.85(2)
P(1)	C(19)	1.86(2)	P(2)	C(5)	1.85(2)
P(2)	C(31)	1.84(2)	P(2)	C(37)	1.82(2)
Fe(1)	Fe(2)	2.611(4)	Fe(1)	P(1)	2.211(6)
Fe(1)	P(2)	2.211(6)	Fe(1)	C(3)	1.76(2)
Fe(2)	C(1)	1.78(2)	Fe(2)	C(2)	1.76(2)
O(1)	C(1)	1.15(2)	O(2)	C(2)	1.16(2)
O(3)	C(3)	1.14(2)	O(4)	C(4)	1.12(2)
Fe(3)	C(43)	1.69(2)	Fe(4)	C(44)	1.73(2)
Fe(4)	C(45)	1.70(3)	Fe(4)	C(46)	1.81(2)

TABLE IV Selected bond angles (Å) for 4a

atom	*atom*	*atom*	*angle*	*atom*	*atom*	*atom*	*angle*
Fe(1)	Se(1)	Fe(2)	66.1(1)	Fe(1)	Se(1)	C(7)	114.6(6)
Fe(2)	Se(1)	C(7)	109.6(6)	Fe(1)	Se(2)	Fe(2)	66.0(1)
Fe(1)	Se(2)	C(25)	116.9(6)	Fe(2)	Se(2)	C(25)	107.3(6)
Fe(1)	P(1)	C(6)	105.5(7)	Fe(1)	P(1)	C(13)	115.9(6)
Fe(1)	P(1)	C(19)	127.2(6)	C(6)	P(1)	C(13)	104.5(9)
C(6)	P(1)	C(19)	98.1(9)	C(13)	P(1)	C(19)	102.3(8)
Se(1)	Fe(1)	Se(2)	82.1(1)	Se(1)	Fe(1)	Fe(2)	57.31(9)
Se(1)	Fe(1)	P(1)	105.5(2)	Se(1)	Fe(1)	P(2)	167.7(2)

TABLE IV (*Continued*)

atom	*atom*	*atom*	*angle*	*atom*	*atom*	*atom*	*angle*
Se(1)	Fe(1)	C(3)	94.1(6)	Se(2)	Fe(1)	Fe(2)	57.25(10)
Se(2)	Fe(1)	P(1)	111.8(2)	Se(2)	Fe(1)	P(2)	92.8(2)
Se(2)	Fe(1)	C(3)	155.9(7)	Fe(2)	Fe(1)	P(1)	158.9(2)
Fe(2)	Fe(1)	P(2)	110.6(2)	Fe(2)	Fe(1)	C(3)	100.8(7)
P(1)	Fe(1)	P(2)	86.7(2)	P(1)	Fe(1)	C(3)	92.2(7)
P(2)	Fe(1)	C(3)	85.9(6)	Se(1)	Fe(2)	Se(2)	81.4(1)
Se(1)	Fe(2)	Fe(1)	56.57(9)	Se(1)	Fe(2)	C(1)	162.7(6)
Se(1)	Fe(2)	C(2)	92.0(5)	Se(1)	Fe(2)	C(4)	98.2(7)
Se(2)	Fe(2)	Fe(1)	56.70(10)	Se(2)	Fe(2)	C(1)	90.4(7)

As seen in Figure 1, the ditertiary phosphine $Ph_2PCH{=}CHPPh_2$ has indeed displaced one axial CO and one equatorial CO from the same iron atom of the parent complex. Additionally, Figure 1 clearly shows that the two phenyl groups are bonded to the two Se atoms in *anti* positions.

The Fe(1)—Fe(2) [2.611(4) Å] distance of **4a** is slightly longer than Fe—Fe bondlengths in similar Se-containing compounds, such as 2.544(2) Å in (μ-PhSe) (μ-PhCH=CH)$Fe_2(CO)_6$,[8] and 2.575(2) Å in (μ-Se2)Fe_2 $(CO)_6$.[11] In the **4a** the bondlengths Fe(1)—Se(1) and Fe(1)—Se(2) (close to the ditertiary phosphine) equal 2.383(3) and 2.388(3) Å, and are slightly shorter than Fe(2)—Se(1) 2.403(3) and Fe(2)—Se(2) 2.403(4) Å (remote from the ditertiary phosphine). The average Fe—Se bondlength of **4a** (2.395 Å) is almost the same as the average Fe—Se bondlengths in (μ-PhSe)(μ-PhCH=CH) $Fe_2(CO)_6$(2.385 Å)[8] and slightly longer than that in (μ-Se_2)$Fe_2(CO)_6$(02.364 Å).[11] It is noteworthy that this is the first crystal structure for a ditertiary phosphine, non-symmetrically substituted, derivative of (μ-RE)$_2Fe_2(CO)_6$(E=S, Se).

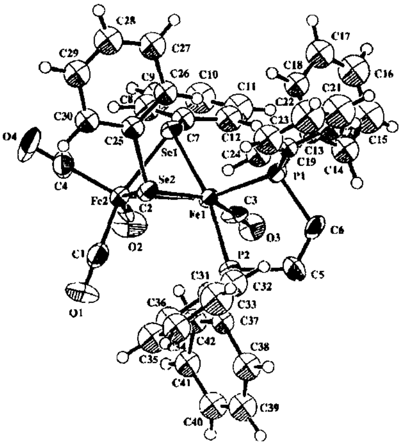


FIGURE 1 Structure of 4a showing the atom numbering scheme.

SUPPLEMENTAL MATERIAL AVAILABLE

Tables of fractional atomic coordinates, thermal parameters, interatomic distances, observed and calculated structure factors are available on request from the authors.

Acknowledgments

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